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8.13 om Krystallinitet, komonomer, og
feltet

bare et metallocen

PCT

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<p>(21) International Application Number: PCT/US98/27361 (22) International Filing Date: 23 December 1998 (23.12.98) (30) Priority Data: 60/068,640 23 December 1997 (23.12.97) US (71) Applicant: UNIVATION TECHNOLOGIES LLC [US/US]; Suite 1950, 5555 San Felipe, Houston, TX 77056 (US). (72) Inventors: MCCULLOUGH, Laughlin, G.; 114 Crystal Reef Drive, League City, TX 77573 (US). CROWTHER, Donna, J.; 1104 Cactus Drive, Baytown, TX 77521 (US). (74) Agents: SHER, Jaimes, Sher et al.; Univation Technologies LLC, Suite 1950, 5555 San Felipe, Houston, TX 77056 (US).</p>	<p>(81) Designated States: CA, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: SLURRY POLYMERIZATION PROCESS WITH ALKYL-SUBSTITUTED BISCYCLOPENTADIENYL METALLOCENES</p>		
<p>(57) Abstract The invention describes a slurry process for producing ethylene polymers and copolymers with high productivity capability that will be particularly suitable for industrial practice. This process relates to contacting ethylene, optionally with one or more copolymerizable monomers, under slurry conditions with a supported zirconium biscyclopentadienyl metallocene wherein at least one cyclopentadienyl group contains a hydrocarbyl or hydrocarbylsilyl group that is a C₄-C₂₀ branched-alkyl or -silylalkyl substituent with said branch occurring at the second or third atom removed from the cyclopentadienyl rings thereof. Examples of poly(ethylene-hexene) made with bis(isobutylcyclopentadienyl) zirconium dichloride and bis(trimethylsilylmethyl)cyclopentadienyl zirconium dichloride are presented with suitable comparisons of similar catalysts.</p>		

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TITLE OF THE INVENTION

Slurry Polymerization Process with Alkyl-substituted Biscyclopentadienyl
Metallocenes

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TECHNICAL FIELD

This invention relates to slurry processes for coordination polymerization
of ethylene containing polyolefins using metallocenes having alkyl-substituted
10 biscyclopentadienyl ligands.

BACKGROUND ART

Metallocene-catalyzed polymerization processes are well known in the art.
15 Such processes employ catalyst systems, which utilize metallocene compounds for
the polymerization of olefinically unsaturated monomers. Metallocene compounds
are defined as organometallic coordination compounds obtained as
cyclopentadienyl derivatives of a transition metal. Processes which employ
multiple metallocenes in a single polymerization reactor are also known. Bridged
20 and unbridged biscyclopentadienyl zirconium metal compounds are particularly
representative; many are said to be useful for ethylene polymerization.
Metallocenes are used as ethylene polymerization catalysts in either supported or
unsupported form.

25 The relative activities of alkyl-substituted metallocenes in olefin
polymerization has been examined in the art. For example, Mar'in, et al. describe
certain ethylene polymerizations using unsubstituted and alkyl-substituted
biscyclopentadienyl zirconium dichlorides in toluene at 70°C and 7.5 atm
ethylene. Among others, bis(*i*-propylcyclopentadienyl) zirconium dichloride and
30 bis(di-*i*-propylcyclopentadienyl) zirconium dichloride were examined. Bis(*i*-
propylcyclopentadienyl) zirconium dichloride was said to exhibit the highest
activity. (See "Alkyl-Substituted Zirconocenes As Components Of A Catalytic

System Of Ethylene Polymerization", Metalloorganicheskaya Khimiya (Organometallic Chemistry), Vol. 3, No. 2, Mar'in, et al., p. 473-474 (1990)).

5 Nekhaeva, et al. also report on ethylene polymerizations using unsubstituted and alkyl-substituted biscyclopentadienyl zirconium dichlorides. Among the metallocenes used were bis(*i*-propylcyclopentadienyl) zirconium dichloride, bis(*n*-propylcyclopentadienyl) zirconium dichloride, bis(*di-i*-propylcyclopentadienyl) zirconium dichloride, bis(cyclohexylcyclopentadienyl) zirconium dichloride, bis(trimethylsilylcyclopentadienyl) zirconium dichloride, and bis(*t*-butylcyclopentadienyl) zirconium dichloride. The trimethylsilyl-substituted metallocene and bis(*i*-propylcyclopentadienyl) zirconium dichloride were said to have the highest activities. Activities of 55,780 kg/mol-catalyst-hr and 17,900 kg/mol-catalyst-hr were reported in Table 1 for bis(*i*-propylcyclopentadienyl) zirconium dichloride and bis(*n*-propylcyclopentadienyl) zirconium dichloride, respectively. (See "Synthesis and Structure of Homo- And Copolymers of Ethylene With Other α -Olefins Obtained By Using Zirconocene Dichloride Derivatives and Methyl Alumoxane", Vysokomolekulyarnye Soedineniya, Vol. (A) 34, No. 1, Nekhaeva, et al, p. 84-91 (1992).)

20 Tait, et al. describe ethylene polymerizations conducted in toluene with biscyclopentadienyl metallocenes of the formula $(\eta^5\text{-RC}_5\text{H}_4)_2\text{ZrCl}_2$, where R is hydrogen, methyl, *n*-propyl, *i*-propyl, and *t*-butyl. In Table 1, the *i*-propyl and *n*-propyl metallocenes are reported to have activities of 9.6 and 9.7 kg PE/mmol Zr-hr, respectively.

25 Metallocenes used in supported form are often illustrated in gas phase polymerization processes where possibly suggesting use in slurry polymerization. For example, PCT International Publication Number WO 93/09148 shows in Table 1 the gas phase polymerization results for supported metallocene catalysts based on, inter alia, bis(*i*-propylcyclopentadienyl) zirconium dichloride, bis(*i*-butylcyclopentadienyl) zirconium dichloride, bis(*n*-propylcyclopentadienyl) zirconium dichloride, and bis(*t*-butylcyclopentadienyl) zirconium dichloride.

In U.S. 5,536,796 (Jejelowo, et al.), gas phase polymerizations using supported isomeric mixtures of 1,2- and 1,3-(dialkylcyclopentadienyl) zirconium dichlorides are reported. Example 9 utilizes an isobutyl-substituted metallocene.

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U.S. 5,608,019 (Cheruvu, et al.) describes gas phase polymerizations utilizing certain silica supported butyl-substituted metallocenes. The use of bis(i-butylcyclopentadienyl) zirconium dichloride is recited in claims 4 and 19.

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Regardless of whether supported or unsupported metallocenes are used, improvements in metallocene polymerization processes are still desired. Metallocenes, compared to transition metal halide polymerization catalysts, are expensive materials. If the metallocene catalyst productivity is too low, the process will not be economical owing to the high catalyst cost. Even if an inexpensive metallocene is used, low productivity will result in high levels of catalyst residue which may require more extensive deashing, contributing to increased costs. These problems are aggravated when metallocene-catalyzed processes are used to make higher density ethylene polymers, such as medium density ethylene/ α -olefin copolymers, high density ethylene/ α -olefin copolymers, and ethylene homopolymers. This is true because metallocene catalysts, like other catalysts, generally exhibit lower catalyst productivity under the polymerization conditions required to make these kinds of products. Productivity is particularly an issue in the manufacture of ethylene homopolymers.

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Thus, there is still a need for supported metallocene-catalyzed ethylene homopolymerization, and medium density copolymerization, and high-density copolymerization slurry processes that operate with higher catalyst productivity. This is especially true for ethylene homopolymerization.

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SUMMARY OF THE INVENTION

The invention is a slurry process for producing ethylene polymers and copolymers. The inventive process exhibits very high productivity and is especially useful for the production of ethylene homopolymers, and for medium density polyethylene (MDPE) or for high-density polyethylene (HDPE). The invention slurry process comprises contacting ethylene, optionally with one or more copolymerizable monomers, under slurry conditions with a supported zirconium biscyclopentadienyl metallocene having on at least one cyclopentadienyl ligand a hydrocarbyl or hydrocarbylsilyl group that is a C₄ - C₂₀ branched-alkyl or silylalkyl substituent with said branching occurring at the second or third atom removed, or away from, the cyclopentadienyl ligand.

In preferred embodiments of the forgoing process the biscyclopentadienyl metallocene is bis(isobutylcyclopentadienyl) zirconium dichloride, bis(1,3-methyl, isobutylcyclopentadienyl) zirconium dichloride and bis(1,2-methyl, isobutylcyclopentadienyl) zirconium dichloride, their isomers and mixtures thereof, bis(2-methylbutylcyclopentadienyl) zirconium dichloride bis(neopentylcyclopentadienyl) zirconium dichloride or bis(trimethylsilylmethyl)cyclopentadienyl) zirconium dichloride, any of their dihydrocarbyl counterparts, such as the dimethyl or dibenzyl analogues, and any of the Group 14 element-containing bridged counterparts, such as those having a covalent bridging group between cyclopentadienyl ligands comprising carbon, silicon or germanium, such as dimethylsilyl(2-methyl,3-trimethylsilylmethyl-indenyl)(cyclopentadienyl) zirconium dichloride.

DETAILED DESCRIPTION OF THE INVENTION

In this patent specification, references to the elemental groups will be made in accordance with the new IUPAC nomenclature for the Periodic Table of Elements, as described in Chemical and Engineering News, 63(5) 27, 1985. Under this convention the groups are numbered 1 to 18.

Metallocenes Useful in the Process of the Invention

The metallocenes utilized in the process of the present invention may be any of the biscyclopentadienyl derivatives of zirconium, provided that at least one of the cyclopentadienyl groups of the biscyclopentadienyl derivative is substituted with a hydrocarbyl or hydrocarbylsilyl group that is a C₄ - C₂₀ branched-alkyl substituent with said branch occurring at the second or third atom removed from the cyclopentadienyl ring. The phrase "second or third atom removed from the cyclopentadienyl ligand" means for the purposes of this specification and claims that there is at least one carbon atom separating the branch point of the branched alkyl substituent from the cyclopentadienyl ring carbon atom having the substituent. Biscyclopentadienyl metallocenes are well known in the art and are characterized by the presence of two cyclopentadienide moieties bonded in an eta-5 fashion to the transition metal. Also suitable are the corresponding bridged cyclopentadienyl compounds. Therefore, in this patent specification the terms "biscyclopentadienyl metallocene," "biscyclopentadienyl zirconium metallocene," and the like shall be understood to refer to and to encompass both unbridged and bridged versions of the respective compounds.

In one embodiment, the cyclopentadienyl rings of the bis(cyclopentadienyl) zirconium metallocenes will be substituted only with one invention branched-alkyl group. In yet another embodiment, at least one cyclopentadienyl group or indenyl group will be substituted with two alkyl groups, one of which is the invention branched-alkyl group and the other of which is a methyl group.

Examples of catalyst systems particularly useful in the process of this invention comprise one or more metallocenes represented by the general formula:



wherein $(C_5R'_k)$ is a substituted cyclopentadienyl, M is zirconium, each group R' may be the same or different and is H or an optionally substituted hydrocarbyl radical such as alkyl, alicyclic, aryl, alkylaryl, or arylalkyl radicals containing from 1 to 20 carbon atoms, a silicon-containing hydrocarbyl radical, or a hydrocarbyl radical wherein two carbon atoms are joined together to form a C₄-C₆ ring, but at least one of said R' is the invention branched-alkyl group; R'' is an optional bridging group is a C₁-C₂₀ alkylene radical, a dihydrocarbyl germanium or silicon, or an alkyl phosphine or amine radical bridging the pair of $(C_5R'_k)$ rings; each Q' can be the same or different and is a hydrocarbyl radical, such as aryl, alkyl, alicyclic, alkenyl, alkylaryl, or arylalkyl having 1-20 carbon atoms, or a hydrocarboxyl radical having 1-20 carbon atoms, or a halogen, or Q' may also be a dihydrocarbyl amido radical.

Exemplary hydrocarbyl radicals are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, cyclohexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, ethylhexyl, phenyl, and the like. Exemplary alkylene radicals are methylene, ethylene, propylene, and the like. Exemplary halogen atoms include chlorine, bromine and iodine and of these halogen atoms, chlorine is preferred.

Methods of substituting hydrocarbon substituents onto a cyclopentadienyl ring of a metallocene are well known, and any suitable method may be utilized. Generally, such methods involve a salt of the cyclopentadienyl compound, such as a lithium or sodium salt, that is reacted with a halogen substituted hydrocarbon substituent. The hydrocarbon substituent becomes covalently bonded to the Cp ring by an SN₂ or substitution reaction, well-known in organic chemistry.

Non-limiting examples of the biscyclopentadienyl metallocenes of the invention include unbridged compounds bis(isobutylcyclopentadienyl) zirconium dichloride, bis(isobutylcyclopentadienyl) zirconium dibromide, bis(isobutylcyclopentadienyl) zirconium diiodide, bis(isobutylcyclopentadienyl) zirconium dimethyl, bis(isobutylcyclopentadienyl) zirconium diethyl,

bis(isobutylcyclopentadienyl) zirconium dipropyl, bis(isobutylcyclopentadienyl) zirconium dibutyl, bis(isobutylcyclopentadienyl) zirconium dibenzyl, bis(1,3-methyl, isobutylcyclopentadienyl) zirconium dichloride, bis(1,2-methyl, isobutylcyclopentadienyl) zirconium dibromide, bis(1,3-methyl, isobutylcyclopentadienyl) zirconium diiodide, bis(1,2-methyl, isobutylcyclopentadienyl) zirconium dimethyl, (1,2-methyl, isobutylcyclopentadienyl)(1,3-methyl, isobutylcyclopentadienyl) zirconium diethyl, bis(1,3-methyl, isobutylcyclopentadienyl) zirconium dibenzyl; and bridged compounds dimethylsilylbis(isobutylcyclopentadienyl) zirconium dichloride, cyclobutylbis(isobutylcyclopentadienyl) zirconium dibromide, diphenylmethyl bis(isobutylcyclopentadienyl) zirconium diiodide, diethylsilylbis(isobutylcyclopentadienyl) zirconium dimethyl, methylphenylmethylbis(isobutylcyclopentadienyl) zirconium dibenzyl, dimethylsilylbis(methylisobutylcyclopentadienyl) zirconium dichloride, diphenylmethylbis(2-methylbutylcyclopentadienyl) zirconium dichloride, diphenylmethylbis(2-ethylbutylcyclopentadienyl) zirconium dichloride, methylphenylmethylbis(neopentylcyclopentadienyl) zirconium dichloride or dimethylsilylbis(trimethylsilylmethylcyclopentadienyl) zirconium dichloride, cyclobutylbis(trimethylsilylmethylcyclopentadienyl) zirconium dimethyl, diphenylmethyl(trimethylsilylmethylcyclopentadienyl) zirconium dichloride, dimethylgermyl (trimethylsilylmethylcyclopentadienyl) zirconium dichloride, and dimethylsilyl(2-methyl,3-trimethylsilylmethyl-indenyl) (cyclopentadienyl) zirconium dichloride; and other permutations of the above with different labile ligands Q' or bridging radicals R", like those illustrated in this listing.

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Catalyst Systems

The catalyst systems of the invention are formed by activating and supporting, in any order, the biscyclopentadienyl metallocenes of the invention. The biscyclopentadienyl metallocenes of the invention may be activated by use of the traditional means of activation, specifically including the use of alkyl alumoxane compounds as activators, and ionizing activators, such as those

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represented by haloaryl-substituted boron or aluminum compounds such as nitrogen-containing salts, carbenium, silylium or phosphonium salts, metal salts and neutral Lewis acid compounds. Each method is well documented in the field of metallocene art. Related means of activation, such as the use of alkyl aluminum or other metal alkyl alkylating agents to convert metallocene halide compounds to hydride or alkyl group-containing compounds prior to activation with the ionizing activator compounds, will be suitable in accordance with the instant invention. For example, it will be understood by those skilled in the art that if ionizing activator compounds are to be used with metallocene halides which do not contain ligands reactive toward ionizing activators, such metallocenes may be treated with alkylating agents to incorporate such reactive ligands, and that this step is one of the steps necessary to form a catalytic complex by ionic activation in these circumstances.

Known alkylaluminum compounds are additionally suitable as catalyst activators, particularly for the invention metal compounds comprising the halide ligands. The alumoxane component useful as catalyst activator typically is an oligomeric aluminum compound represented by the general formula $(R-Al-O)_{[n]}$, which is a cyclic compound, or $R(R-Al-O)_{[n]}AlR_2$, which is a linear compound. In the general alumoxane formula R is a C_1 to C_5 alkyl radical, for example, methyl, ethyl, propyl, butyl or pentyl and "n" is an integer from 1 to about 50. Most preferably, R is methyl and "n" is at least 4. Alumoxanes can be prepared by various procedures known in the art. For example, an aluminum alkyl may be treated with water dissolved in an inert organic solvent, or it may be contacted with a hydrated salt, such as hydrated copper sulfate suspended in an inert organic solvent, to yield an alumoxane. Generally, however prepared, the reaction of an aluminum alkyl with a limited amount of water yields a mixture of the linear and cyclic species of the alumoxane.

For purposes of this patent specification the terms "carrier" or "support" are interchangeable and can be any support material, preferably a porous or microporous support material, such as for example, talc, inorganic oxides,

inorganic chlorides, for example magnesium chloride and resinous support materials such as polystyrene, polyolefin or polymeric compounds, or any other organic support material, and the like, that has an average particle size greater than 10 μm .

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The immobilized catalyst systems of the invention may be prepared by any effective method of supporting other coordination catalyst systems, effective meaning that the catalyst so prepared can be used for preparing polymer in a heterogeneous olefin polymerization process. Preferred methods include those referred to in WO 96/00245. In accordance with this method, as illustrated in the examples below, the transition metal compound is combined with an activator compound in solvent to prepare a precursor solution which is added to a porous support particle in such a manner that the total solvent volume exceeds the total particle pore volume but is less than that at which the formation of a slurry is observed.

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The activated catalyst may also be supported in accordance with WO 91/0882 and WO 94/03506, particularly when using ionizing activators providing electronically stabilizing non-coordinating anions. In this method, inorganic oxide particle supports are treated with a Lewis acid to neutralize any hydroxyl groups remaining on the surfaces after thorough drying and prior to the adsorption of the activated catalyst complex from the solution in which it is added.

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The support method in WO 96/08520 will also be suitable in accordance with this invention.

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Additional methods appear in the following descriptions for metallocene catalysts, these methods will be suitable as well for the invention catalyst systems. U.S. Patent No. 4,937,217 generally describes a mixture of trimethylaluminum and triethylaluminum added to an undehydrated silica to which a metallocene catalyst component is then added. EP-308177-B1 generally describes adding a wet monomer to a reactor containing a metallocene, trialkylaluminum and

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undehydrated silica. U.S. Patent Nos. 4,912,075, 4,935,397 and 4,937,301 generally relate to adding trimethylaluminum to an undehydrated silica and then adding a metallocene to form a dry supported catalyst system. U.S. Patent No. 4,914,253 describes adding trimethylaluminum to undehydrated silica, adding a metallocene and then drying the resulting supported catalyst system with an amount of hydrogen to produce a polyethylene wax. U.S. Patent Nos. 5,008,228, 5,086,025 and 5,147,949 generally describe forming a dry supported catalyst system by the addition of trimethylaluminum to a water impregnated silica to form alumoxane in situ and then adding the metallocene. U.S. Patent Nos. 4,808,561, 4,897,455 and 4,701,432 describe techniques to form a supported catalyst where the inert carrier, typically silica, is calcined and contacted with a metallocene(s) and an activator/cocatalyst component. U.S. Patent No. 5,238,892 describes forming a dry supported catalyst system by mixing a metallocene with an alkyl aluminum and then adding undehydrated silica. U.S. Patent No. 5,240,894 generally pertains to forming a supported metallocene/alumoxane catalyst system by forming a metallocene/alumoxane reaction solution, adding a porous carrier, and evaporating the resulting slurry to remove residual solvent from the carrier.

Polymeric carriers will also be suitable in accordance with the invention, see for example the descriptions in WO 95/15815 and U.S. patent 5,427,991. As taught for metallocene catalysts in these documents, the catalyst complexes of this invention may be either adsorbed or absorbed, on the polymeric supports, particularly if made up of porous particles, or may be chemically bound through functional groups covalently bound to or in the polymer chains. See also, International application PCT/US98/11696.

The preferred inorganic oxide materials are those which are selected from the Periodic Table of Elements of Groups 2, 3, 4, 5, 13 or 14 metal or metalloid oxides. In a preferred embodiment, the catalyst support materials include silica, alumina, silica-alumina, and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, alumina or silica-alumina are magnesia, titania, zirconia, and the like.

It is preferred that the inorganic oxide carriers of the catalyst of this invention have a surface area in the range of from about 10 to about 700 m²/g, pore volume in the range of from about 0.1 to about 4.0 cc/g and average particle size in the range of from about 10 to about 500 μm. More preferably, the surface area is in the range of from about 50 to about 500 m²/g, pore volume of from about 0.5 to about 3.5 cc/g and average particle size of from about 20 to about 200 μm. Most preferably the surface area range is from about 100 to about 400 m²/g, pore volume from about 0.8 to about 3.0 cc/g and average particle size is from about 30 to about 100 μm. The pore size of the carrier of the invention typically has pore size in the range of from 10 to 1000 Angstroms, preferably 50 to about 500 Angstroms, and most preferably 75 to about 350 Angstroms. Polymeric supports will preferably have even lower surface areas, particularly when the catalyst of the invention are activated with the haloaryl-substituted boron or aluminum compounds.

The above documents typically discuss specific methods of supporting metallocene catalysts. Generally the procedures that follow will be suitable. An aluminoxane, such as methylaluminumoxane or modified aluminumoxane, or other suitable cocatalyst activator such as Al(CH₃)₃, Al(CH₂CH₃)₂Cl, B(C₆F₅)₃, [C₆H₅NMe₂H]⁺[B(C₆F₅)₄]⁻, [(C₆H₅)₃C]⁺[B(C₆F₅)₄]⁻, [H]⁺[PF₆]⁻, [Ag]⁺[BF₄]⁻, [Ag]⁺[PF₆]⁺, or [Ag]⁺[B(C₆F₅)₄]⁻ is combined with one or more transition metal complexes in an appropriate solvent to form a precursor solution. A suitable support, preferably porous, is charged to a vessel and the precursor solution is added with stirring. The mixture may be mixed by hand with a spatula, by a rotating stirrer with wire loops such as a Kitchen Aid dough mixer, by metal blades rotating at high speed such as in a Wehring blender, by a helical ribbon bladed mixer, by shaking, tumbling, fluidized bed mixing, by paddle or propeller blades on a rotating stir shaft, or other appropriate means. The total amount of solvent used to form the precursor suspension or solution may be less than the pore volume of the support as in impregnation to incipient wetness, or greater than the pore volume of the support such that a slurry is formed, or an amount in

between such that a solution-finely divided support mixture is neither free flowing nor a slurry. Solution may be added to support or vice versa as appropriate to the mixing method. If desired the liquids may be removed by purging with an inert gas or under vacuum.

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When using the activated, supported catalysts of the invention, the total catalyst system will generally additionally comprise one or more scavenging compounds. The term "scavenging compounds" as used in this application is meant to include those compounds effective for removing polar impurities from the reaction solvent. Such impurities can be inadvertently introduced with any of the polymerization reaction components, particularly with solvent, monomer and catalyst feed, and adversely affect catalyst activity and stability. It can result in decreasing or even elimination of catalytic activity, particularly when a metallocene cation-noncoordinating anion pair is the catalyst system. The polar impurities, or catalyst poisons include water, oxygen, metal impurities, etc. Preferably steps are taken before provision of such into the reaction vessel, for example by chemical treatment or careful separation techniques after or during the synthesis or preparation of the various components, but some minor amounts of scavenging compound will still normally be required in the polymerization process itself. Typically the scavenging compound will be an organometallic compound such as the organometallic compounds of U.S. Pat. Nos. 4,701,432, 5,153,157, 5,241,025, EP-A- 638 697 and WO-A-91/09882 and WO-A-94/03506, noted above, and that of WO-A-93/14132. Exemplary compounds include triethyl aluminum, triethyl borane, tri-isobutyl aluminum, isobutyl aluminumoxane, and n-octyl aluminum, those having bulky substituents covalently bound to the metal or metalloid center being preferred to minimize adverse interaction with the active catalyst. When an alkyl aluminum or alumoxane is used as activator, any excess over the amount of metallocene present will act as scavenger compounds and additional scavenging compounds may not be necessary. The amount of scavenging agent to be used with metallocene cation-noncoordinating anion pairs is minimized during polymerization reactions to that amount effective to enhance

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activity. If the amount is too great or contact time is too long, detrimental catalyst deactivation might occur.

Polymerization Process

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Slurry polymerization processes in which the immobilized catalyst systems of this invention may be used are typically described as those in which the polymerization medium can be either a liquid monomer, like propylene, or a hydrocarbon solvent or diluent, advantageously aliphatic paraffin such as propane,
10 isobutane, hexane, heptane, cyclohexane, etc. or an aromatic one such as toluene. The inventive process may be carried out in batch mode, semi-batch mode, or, preferably, continuously. Industrially practiced continuous, loop slurry processes will be preferred for commercial reasons. The polymerization temperatures may be those considered low, e.g., less than 50 °C, preferably 0 - 30 °C, or may be in a
15 higher range, such as up to about 150 °C, preferably from 50 °C up to about 80 °C, or at any ranges between the end points indicated. Pressures can vary from about 100 to about 700 psia (0.76-4.8 MPa). Additional description is given in U.S. patents 5,274,056 and 4,182,810, and in International publications WO 94/21962 and WO 97/24375, all of which are incorporated by reference for
20 purposes of U.S. patent practice.

In one embodiment ethylene alone is polymerized, that is no comonomer is added, to form an ethylene homopolymer. For copolymers, the optional
25 comonomer, which will typically be a copolymerizable olefin, is provided to the polymerization process and thus incorporated into the growing polymer chain to disrupt ethylene crystallinity and thereby modify the properties of the polymer. As is well known, when comonomer is provided to the process, a comonomer to ethylene ratio is established, and as more comonomer is provided relative to the ethylene, this ratio becomes higher and more comonomer is incorporated into the
30 polymer with the result that the polymer crystallinity and density is lowered. Polymer density is a direct measure of polymer crystallinity and can be determined using standardized methods well known to the art. Thus, by

controlling the relative amounts of comonomer and ethylene provided to the polymerization process, the density of the polymers produced may be adjusted to the desired levels.

5 In the inventive process, the provided comonomer serves to lower the density of the polymer below that observed for the corresponding ethylene homopolymer, which is prepared in the absence of comonomer. Higher ratios of comonomer to ethylene will produce lower density polymers and the ratio of
10 determined by those skilled in the art. For example, in continuous ethylene polymerization operations, the density of the polymer being produced is typically regularly measured by securing samples of the polymer as it is discharged from the process, drying the samples if necessary, and measuring the density of the samples according to well known methods, such as, for example, those set forth in
15 ASTM D 1505. By noting the trends in the density of the polymer samples over time, more or less comonomer can be provided to the process, thereby adjusting the ratio of comonomer to ethylene in the process to produce a polymer having the desired density. Similar procedures are used in batch polymerization processes, where varying ratios of comonomer to ethylene would typically be established in
20 the process near the outset of the polymerization run, and, if necessary, adjusted either upward or downward in the next run according to the density results obtained. The ratio of comonomer to ethylene can be measured using techniques and equipment well known in the art, for example on-line gas chromatography.

25 Suitable comonomers for the process of the instant invention are the olefinically unsaturated compounds which include, for example, the $C_1 - C_{20}$ α -olefins such as 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene; and branched 1-olefins such as 3 methyl-1-butene, 3-methyl-1-pentene and 4-methyl-styrene-1-pentene, and vinyl- or vinylidene-terminated polymers and
30 oligomers such as those having up to 250 carbon atoms and higher. Cyclic olefins will also be suitable, especially C_5 to C_{20} cyclic olefins including cyclopentene, norbornene, methylnorbornene, ethylnorbornene, and cyclododecene. Vinyl

aromatics, e.g., styrene and alkyl-substituted styrenes are also suitable.

The process in accordance with the invention is particularly useful for the production of high density and medium density ethylene polymers. Medium density ethylene polymers, known as medium density polyethylene (MDPE), are defined herein as those polymers having densities equal to or greater than 0.915, but less than 0.940 g/cc. High density ethylene polymers, which are traditionally known as high-density polyethylene (HDPE), are defined herein to include those grades where the density is equal to or above 0.940 g/cc up to about 0.970 g/cc. Preferably the MDPE polymers made by the inventive process will have a density equal to or greater than 0.925 g/cc, but less than 0.940, more preferably equal to or greater than about 0.930, but less than 0.940 g/cc, and still more preferably greater than or equal to about 0.935, but less than 0.940 g/cc. Preferably the HDPE polymers made by the inventive process will have a density equal to or greater than 0.940 g/cc, more preferably equal to or greater than about 0.945 g/cc, and most preferably greater than or equal to about 0.950 g/cc. Most preferably the polymers will be ethylene homopolymers. As used herein in connection with polymer density, "about" means within plus or minus 0.002 g/cc.

Thus, in one embodiment, the process of the invention further comprises adjusting the ratio of comonomer to ethylene in the process to produce a polymer having a density greater than about 0.925 g/cc, preferably greater than about 0.930, more preferably greater than about 0.935, even more preferably greater than about 0.940 g/cc, yet more preferably greater than about 0.945 g/cc, and most preferably greater than or equal to about 0.950 g/cc. Another embodiment of the present invention is the process as defined above wherein no comonomer is contacted with the ethylene and the metallocene, that is ethylene alone is fed to the reaction medium in order to form an ethylene homopolymer.

The feedstock purification prior to introduction into the reactor follows standard practices in the art, e.g. molecular sieves, alumina beds and oxygen

removal catalysts are used for the purification of ethylene, alpha -olefin, and optional diene. The solvent or diluent itself as well are similarly treated.

The α -olefin monomer(s) and diene monomer(s), if included, are introduced in an amount proportional to the levels of incorporation desired for the polymer to be produced and the effective reactive ratios for the polymerizable monomers in the presence of the specific catalyst chosen. In the preferred embodiment the combination of the α -olefin monomer(s) in reaction solvent as introduced into the reactor and effective vapor pressure of the α -olefin monomer(s) is maintained according to the rate of incorporation into the copolymer product. In an alternative embodiment, the partial pressure in the reactor will be provided by ethylene alone in which situation the α -olefin monomer(s) are added solely with reaction solvent. The amounts and vapor pressure will vary according to catalyst selection and polymer to be produced, but can be empirically determined well within the skill in the art, particularly in view of the description provided in the following examples.

The scavenging compounds are provided separately afterwards or with one of the foregoing feedstreams, in an amount suitable to increase the activity of the catalyst but in an amount lower than that at which depression of reactivity is observed. Typically an effective amount of the scavenging compound is about 0 (e.g., with an alumoxane activator) to 100 mol. ratio based upon the ratio of scavenging compound to activator, preferably the ratio is 0.3 to 30, and most preferably it is 0.5 to 10.

Ethylene is provided into the reaction vessel in an amount proportional to the level of incorporation desired and the effective reactive ratios for the polymerizable monomers in the presence of the specific catalyst chosen, as with the alpha -olefin monomer(s). The polymerization starts upon contact of the monomers with the activated, supported catalyst. In the examples below, ethylene-1-hexene copolymers were prepared using catalysts of the invention and comparative catalysts in order to illustrate the surprising activities illustrated by

the claimed catalysts. The abbreviations used are: Cp = cyclopentadienyl; i-Bu = isobutyl; n-Bu = normalbutyl; t-Bu = tertiarybutyl; i-Pr = isopropyl; Et = ethyl; Me = methyl; and MAO = methylalumoxane.

5 Though the Examples and the discussion are directed to a single reactor configuration and narrow polydispersity polymers, it is well-known that the use in series of two reactors, e.g., batch or tubular, or combined in series or parallel, each operated so as to achieve different polymer molecular weight characteristics, or by blending polymers from different reactors or reactor conditions, or utilizing two or more different transition metal catalysts in one or more reactors, can yield
10 improved processing polymers.

EXAMPLES

1. Preparation of supported bis(isobutylcyclopentadienyl)zirconium dichloride. 37.24 g of 30 wt% MAO in toluene and 39.00 g toluene were
15 combined to give a clear, colorless solution. The mixture was stirred 15 minutes, then 0.649 g bis(isobutylcyclopentadienyl)zirconium dichloride was added to give a yellow solution. The reaction was stirred 15 minutes, then 30.00 g Davison 948 silica (50 μ , dried at 600°C) was then added and the resulting thick mixture was stirred by hand for 10 minutes using a spatula. The mixture was dried 20 hours *in*
20 *vacuo* to give 42.58 g light yellow solid.

2. Preparation of supported bis(butylcyclopentadienyl)zirconium dichloride. Bis(n-butylcyclopentadienyl) zirconium dichloride was supported in a manner similar to bis(isobutylcyclopentadienyl)zirconium dichloride using 37.24
25 g of 30 wt% MAO and 0.649 g bis(butylcyclopentadienyl)zirconium dichloride, which yielded 42.36 g yellow, free-flowing solid.

3. Preparation of supported bis(*t*-butylcyclopentadienyl)zirconium dichloride. Bis(*t*-butylcyclopentadienyl) zirconium dichloride was supported in a
30 manner similar to bis(isobutylcyclopentadienyl)zirconium dichloride using 37.24

g of 30 wt% MAO and 0.649 g bis(*t*-butylcyclopentadienyl)zirconium dichloride, which yielded 41.55 g light yellow, free-flowing solid.

4. Preparation of supported bis(isopropylcyclopentadienyl)zirconium dichloride. Bis(isopropylcyclopentadienyl) zirconium dichloride was supported in a manner similar to bis(isobutylcyclopentadienyl)zirconium dichloride using 37.18 g of 30 wt% MAO and 0.603 g bis(isopropylcyclopentadienyl)zirconium dichloride, which yielded 42.23 g light yellow, free-flowing solid.

5. Preparation of supported bis(trimethylsilylcyclopentadienyl)zirconium dichloride. Bis(trimethylsilylcyclopentadienyl)zirconium dichloride was supported in a manner similar to bis(isobutylcyclopentadienyl)zirconium dichloride using 37.30 g of 30 wt% MAO and 0.702 g bis(trimethylsilylcyclopentadienyl)zirconium dichloride, which yielded 41.35 g light yellow tan solid.

6. Preparation of supported bis(trimethylsilylmethylcyclopentadienyl)zirconium dichloride. Bis(trimethylsilylmethylcyclopentadienyl)zirconium dichloride was supported in a manner similar to bis(isobutylcyclopentadienyl)zirconium dichloride using 37.36 g of 30 wt% MAO and 0.748 g bis(trimethylsilylmethylcyclopentadienyl)zirconium dichloride, which yielded 42.51 g yellow, free-flowing solid.

7. Preparation of supported bis(ethylcyclopentadienyl)zirconium dichloride. Bis(ethylcyclopentadienyl)zirconium dichloride was supported in a manner similar to bis(isobutylcyclopentadienyl)zirconium dichloride using 6.19 g of 30 wt% MAO, 6.50 g toluene, 0.093 g bis(ethylcyclopentadienyl)zirconium dichloride and 5.00 g Davison 948 silica, which yielded 6.76 g light yellow, free-flowing solid.

8. Slurry polymerizations using supported bis(isobutylcyclopentadienyl)zirconium dichloride. To a jacketed, stainless steel 1 liter autoclave previously

purged with hot nitrogen and equipped with an inclined-blade impeller and a baffle was added 400 mL isobutane and 30 mL 1-hexene containing 15 μ L triethylaluminum. The autoclave was stirred and equilibrated at 85°C. 25 mg supported bis(isobutylcyclopentadienyl)zirconium dichloride catalyst was injected
5 into the autoclave using ethylene pressure. The polymerization was maintained at 130 psi ethylene and 85°C for 40 minutes, then the autoclave was vented, cooled and opened. The polymer was isolated, stabilized with 0.15 wt% Irganox B561, and dried overnight under vacuum at 60°C. The yields for five runs were 64.13 g, 55.93 g, 60.39 g, 49.77 g, and 59.03 g.

10

9. Slurry polymerizations using supported bis(butylcyclopentadienyl)zirconium dichloride. (Comparative) Three polymerizations run under the same conditions used for supported bis(isobutylcyclopentadienyl)zirconium dichloride except using 25 mg supported
15 bis(butylcyclopentadienyl)zirconium dichloride yielded 71.04 g, 81.47 g, and 74.81 g of polymer.

10. Slurry polymerizations using supported bis(*t*-butylcyclopentadienyl)zirconium dichloride. (Comparative) Two polymerizations run under the same
20 conditions used for supported bis(isobutylcyclopentadienyl)zirconium dichloride except using 150 mg supported bis(*t*-butylcyclopentadienyl)zirconium dichloride yielded 5.66 g and 6.37 g of polymer.

11. Slurry polymerizations using supported bis(isopropylcyclopentadienyl)zirconium dichloride. (Comparative) Three
25 polymerizations run under the same conditions used for supported bis(isobutylcyclopentadienyl)zirconium dichloride except using 25 mg supported bis(isopropylcyclopentadienyl)zirconium dichloride yielded 10.12 g, 10.10 g, and 9.91 g of polymer.

30

12. Slurry polymerizations using supported bis(ethylcyclopentadienyl)zirconium dichloride. (Comparative) Three polymerizations run under the same

conditions used for supported bis(isobutylcyclopentadienyl)zirconium dichloride except using 25 mg supported bis(isopropylcyclopentadienyl)zirconium dichloride yielded 21.14 g, 20.33 g, and 19.37 g of polymer.

5 13. Slurry polymerizations using supported
bis(trimethylsilylcyclopentadienyl) zirconium dichloride. (Comparative) Four
polymerizations run under the same conditions used for supported
bis(isobutylcyclopentadienyl)zirconium dichloride except using 150 mg supported
bis(trimethylsilylcyclopentadienyl)zirconium dichloride yielded 28.32 g, 26.89 g,
10 17.18 g, and 25.74 g of polymer.

 14. Slurry polymerizations using supported bis(trimethylsilylmethyl-
cyclopentadienyl) zirconium dichloride. Three polymerizations run under the
same conditions used for supported bis(isobutylcyclopentadienyl)zirconium
15 dichloride except using 25 mg supported
bis(trimethylsilylmethylcyclopentadienyl)zirconium dichloride yielded 79.02 g,
80.24 g, and 69.29 g of polymer.

The results of the foregoing examples, with measured average activity
20 based on gram polymer produced per gram-hour of supported catalyst used (g/g
hr), are presented in Table 1 below. It is apparent that though bis(n-
butylcyclopentadienyl) zirconium dichloride (ex. 9) illustrates a higher activity
than the bis(i-butylcyclopentadienyl) zirconium dichloride in this series of
polymerization runs, the branched alkyl-substituent invention embodiments (exs.
25 8 and 14) are much higher than the closest structural analogs, and much closer in
performance to the linear alkyl-substituted embodiment than any of the other
comparatives. The invention embodiment of example 14,
bis(trimethylsilylmethylcyclopentadienyl)zirconium dichloride, even exceeded the
average performance of the example 9 embodiment.

TABLE I. Slurry Data

Ex.	Catalyst *	Amount	Yield	Activity	Avg. Activity
8-a	(i-BuCp) ₂ ZrCl ₂	25 mg	64.13 g	3848 (g/g hr)	3471±324 (g/g hr)
8-b	(i-BuCp) ₂ ZrCl ₂	25 mg	55.93 g	3356 (g/g hr)	
8-c	(i-BuCp) ₂ ZrCl ₂	25 mg	60.39 g	3623 (g/g hr)	
8-d	(i-BuCp) ₂ ZrCl ₂	25 mg	49.77 g	2986 (g/g hr)	
8-e	(i-BuCp) ₂ ZrCl ₂	25 mg	59.03 g	3542 (g/g hr)	
9-a	(n-BuCp) ₂ ZrCl ₂ (Comp)	25 mg	71.04 g	4262 (g/g hr)	4546±317 (g/g hr)
9-b	(n-BuCp) ₂ ZrCl ₂	25 mg	81.47 g	4888 (g/g hr)	
9-c	(n-BuCp) ₂ ZrCl ₂	25 mg	74.81 g	4489 (g/g hr)	
10-a	(t-BuCp) ₂ ZrCl ₂ (Comp)	150 mg	5.66 g	57 (g/g hr)	61±5 (g/g hr)
10-b	(t-BuCp) ₂ ZrCl ₂	150 mg	6.37 g	64 (g/g hr)	
11-a	(i-PrCp) ₂ ZrCl ₂ (Comp)	25 mg	10.12 g	610 (g/g hr)	604±8 (g/g hr)
11-b	(i-PrCp) ₂ ZrCl ₂	25 mg	10.10 g	606 (g/g hr)	
11-c	(i-PrCp) ₂ ZrCl ₂	25 mg	9.91 g	595 (g/g hr)	
12-a	(EtCp) ₂ ZrCl ₂ (Comp)	25 mg	21.14 g	1268 (g/g hr)	1217±53 (g/g hr)
12-b	(EtCp) ₂ ZrCl ₂	25 mg	20.33 g	1220 (g/g hr)	
12-c	(EtCp) ₂ ZrCl ₂	25 mg	19.37 g	1162 (g/g hr)	
13-a	(Me ₃ SiCp) ₂ ZrCl ₂ (Comp)	150 mg	28.32	283 (g/g hr)	245±50 (g/g hr)
13-b	(Me ₃ SiCp) ₂ ZrCl ₂	150 mg	26.89	269 (g/g hr)	
13-c	(Me ₃ SiCp) ₂ ZrCl ₂	150 mg	17.18	172 (g/g hr)	
13-d	(Me ₃ SiCp) ₂ ZrCl ₂	150 mg	25.74	257 (g/g hr)	
14-a	(Me ₃ SiCH ₂ Cp) ₂ ZrCl ₂	25 mg	79.02	4741 (g/g hr)	4571±360 (g/g hr)
14-b	(Me ₃ SiCH ₂ Cp) ₂ ZrCl ₂	25 mg	80.24	4814 (g/g hr)	
14-c	(Me ₃ SiCH ₂ Cp) ₂ ZrCl ₂	25 mg	69.29	4157 (g/g hr)	

* note : The catalyst concentration for all runs was 8.4 μmol Zr/g supported catalyst

5 We claim :

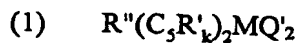
CLAIMS :

1. A slurry process for producing ethylene polymers and copolymers comprises contacting ethylene, optionally with one or more copolymerizable monomers, under slurry conditions with a supported zirconium bicyclopentadienyl metallocene having on at least one cyclopentadienyl ligand, a hydrocarbyl or hydrocarbylsilyl group that is a C₄ - C₂₀ branched-alkyl or -silylalkyl substituent with the branching occurring at the second or third atom removed from the cyclopentadienyl ring carbon thereof.
2. The process of claim 1 wherein said metallocene is bis(isobutylcyclopentadienyl) zirconium dichloride or bis(isobutylcyclopentadienyl) zirconium dimethyl.
3. The process of claim 1 wherein said metallocene is selected from one or more of bis(1,3-methyl, isobutylcyclopentadienyl) zirconium dichloride, bis(1,2-methyl, isobutylcyclopentadienyl) zirconium dichloride, bis(2-methylbutylcyclopentadienyl) zirconium dichloride, bis(neopentylcyclopentadienyl) zirconium dichloride, bis(trimethylsilylmethyl)cyclopentadienyl) zirconium dichloride dimethylsilyl(2-methyl,3-trimethylsilylmethyl-indenyl)(cyclopentadienyl) zirconium dichloride, or any of their dihydrocarbyl counterparts.
4. The process of any of claims 1-3 wherein the temperature of said reaction medium is between 40 °C and 150 °C.
5. The process of any of claims 1-4 wherein said activator comprises a haloaryl-substituted boron or aluminum compound.
6. The process of any of claims 1-4 wherein said activator comprises an alkyl alumoxane compound.

7. The process of any of claims 1-6 wherein said ethylene is polymerized with at least one C₃-C₈ α-olefin.

8. The process of any of claims 1-6 wherein said ethylene is polymerized, optionally with at least one C₃-C₈ α-olefin, to prepare an ethylene copolymer having a density greater than 0.915 and less than about 0.970.

9. The process of any of claims 1-8 wherein said metallocene is one or more metallocenes represented by the general formula:



wherein (C₅R'_k) is a substituted cyclopentadienyl, M is zirconium, each group R' may be the same or different and is H or an optionally substituted hydrocarbyl radical such as alkyl, alicyclic, aryl, alkylaryl, or arylalkyl radicals containing from 1 to 20 carbon atoms, a silicon-containing hydrocarbyl radical, or a hydrocarbyl radical wherein two carbon atoms are joined together to form a C₄-C₆ ring, but at least one of said R' is said branched-alkyl substituent; R'' is an optional bridging group selected from C₁-C₂₀ alkylene radical, a dihydrocarbyl germanium or silicon radical bridging the pair of (C₅R'_k) rings; each Q' can be the same or different and is a hydrocarbyl radical, such as aryl, alkyl, alicyclic, alkenyl, alkylaryl, or arylalkyl having 1-20 carbon atoms, or a hydrocarboxyl radical having 1-20 carbon atoms, or a halogen.

10. The process of claim 1 where used to prepare an ethylene copolymer having a density greater than 0.915 and less than about 0.970.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/27361

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C08F10/02 C08F4/642 C08F2/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of box C. Patent family members are listed in annex.

*** Special categories of cited documents :**

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p>
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Date of the actual completion of the international search	Date of mailing of the international search report
28 April 1999	10/05/1999

Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Gamb, V
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/27361

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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